

UCRL- 93732
PREPRINT


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To Be Published In
Joint Symposium on Swarm Studies and
Inelastic Electron - Molecule Collisions

ed. by
A. Chutjian, V. McKoy,
L.C. Pitchford, and S. Trajmar

November 20, 1985



Lawrence
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ELECTRON-ION RECOMBINATION IN HIGH PRESSURE GASES

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Abstract

This paper reviews recent experimental and theoretical research on recombination of electrons and ions in molecular gases at high pressure.

Introduction

Recombination of electrons and ions in low pressure gases has been reviewed extensively in the past (see, for example Ref. 1). Theoretical treatments of the effects of neutral gas pressure on recombination [2,3] preceded experimental observation [4] of such effects. The process being discussed here is neutral stabilized collisional radiative recombination in which the recombining electron loses energy in collisions (elastic or inelastic) with atoms or molecules. The state of ionic recombination theory through 1975 has been ably reviewed by Flannery [5]. (Note that Bates [6] has very recently reviewed the theory of ion-ion recombination, a process possessing much of the same physics being discussed here). Since 1979 there has been a flurry of both experimental and theoretical research on electron recombination in high pressure molecular gases where inelastic electron-molecular collisions serve to enhance recombination rates. This research is the subject of this review.

Recombination at Moderate Pressures

Warman, Sennhauser, and Armstrong [7,8] have measured electron recombination rate coefficients as functions of pressure in a variety of molecular gases. The recombination rates were obtained by microwave absorption measurement of the decay of conductivity after pulse

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ionization. Their measured values of α ($\text{cm}^3 \text{ s}^{-1}$) the total recombination rate coefficient, for CO_2 , H_2O , and NH_3 are shown in Fig. 1.

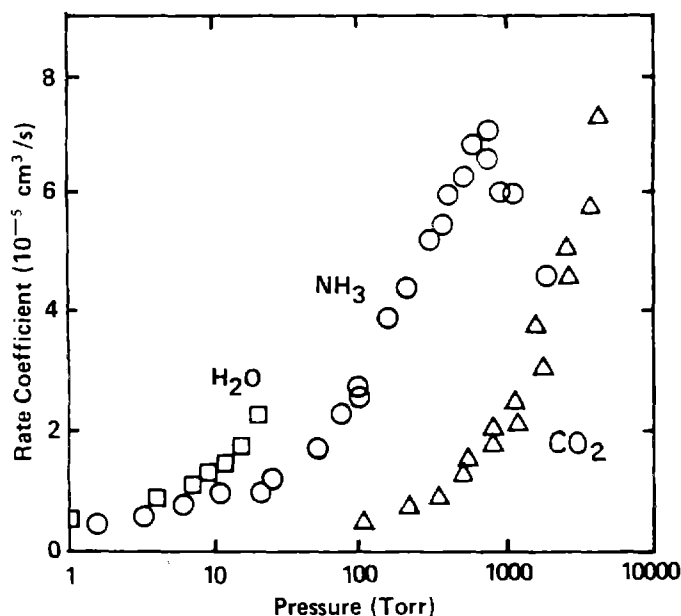


Figure 1. Measured recombination rate coefficients for electrons in molecular gases [7,8].

At pressures below that of the maximum rate coefficient α increases linearly with pressure. This is the region that is most difficult to describe theoretically. At high pressures the rate of recombination is simply limited by the rate at which electrons diffuse toward ions. This process, studied variously by Langevin, Harper, and Debye in the older literature and discussed recently from a new perspective by Bates [9,10], is described by the simple relation,

$$\alpha_D = 4\pi e\mu/\epsilon \quad (1)$$

where μ is the electron mobility and ϵ is the dielectric constant.

Theory of recombination below the diffusion limit.
Warman, et al. [7] and Phelps [11] have proposed a model

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that is useful in estimating α and in illuminating the physics of the recombination process. Assuming that $\alpha = \alpha_2 + \alpha_3 N$ where α_2 is a two body dissociative recombination rate and α_3 is a three body rate (N is the gas density) they proposed writing

$$\alpha_3 = C r_T^3 (\nu_u/N) \quad (2)$$

This expression is based on similar formulae derived by Massey and Burhop [12] ($C = 4\pi/3$) in analogy to Thomson ion-ion recombination theory (see Refs. 5 and 6) and by Pitaevskii [13] ($C = 9\pi$) from diffusion theory for recombination in a monatomic gas. Here $r_T = 2e^2/3kT$ is the Thomson radius. The experimentally measurable parameter ν_u/N is the energy exchange collision frequency [14] defined by

$$\nu_u/N = \frac{e(\mu N) (E/N)^2}{\epsilon_K - kT} \quad (3)$$

where ϵ_K is the characteristic energy, which is related to the mobility and the diffusion coefficient by $\epsilon_K = eD/\mu$. The rate of energy exchange by electrons is expressed in terms of this collision frequency by [14]

$$-\frac{d\bar{u}}{dt} = (\nu_u/N) (\epsilon_K - kT) N$$

Experimental values of D and μ as functions of E/N are available for many gases [15].

Fig. 2 [16] shows the predictions of eqn. (2) with the Massey and Burhop and the Pitaevskii constants. Some theoretical and measured values of α_3 are also plotted in Fig. 2. Additional theoretical values for the rare gases based on the Bates and Khan theory [2] are given in Ref. [22]. We see that the simple model expressed by eqn. (3) yields the correct qualitative trend in α_3 as a function of transport coefficients. Considering the simplicity of the model, the quantitative estimates of α_3 are reasonable. There are two major deficiencies of this model. First, ν_u/N is sometimes a steep function of ϵ_K so that α_3 is sensitive to the

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choice of ϵ_K . It is not even clear what the best method of choosing ϵ_K is. Second, D and μ are defined for constant electric fields and steady state conditions whereas the recombination process below the diffusion limit involves strong fields and steep gradients.

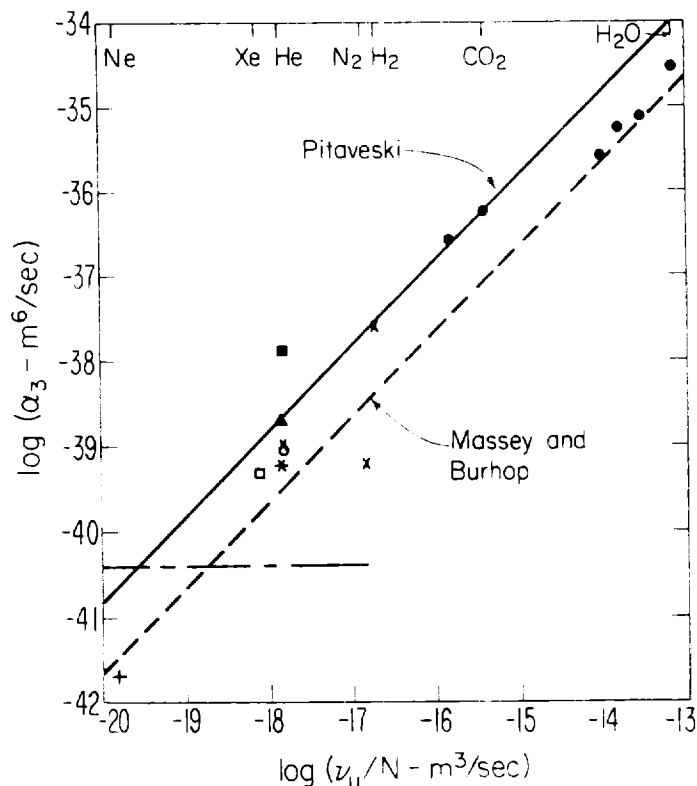


Figure 2. Three body recombination rate coefficients versus energy exchange collision frequency. The references to the points plotted are: X [2,3], ● [7], ▲ [17], ■ [18], + [19], ○ [20], * [21]. Reproduced with permission [16].

Computer simulations of recombination. Computer simulation, which has been very useful in the study of ion-ion recombination (see Ref. [6] and the references contained therein), has been applied to the modeling of electron-ion recombination by Morgan and Bardsley [23] and by Morgan [24,25]. Two types of simulation have been used. First are Monte Carlo (MC) simulations [23,24] that

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compute the classical trajectories of electrons approaching ions from afar until they either recombine or escape. This is just the two body central force problem plus elastic and inelastic collisions between electrons and molecules. The second kind of simulation is molecular dynamics (MD) [25] in which 50 mutually interacting electron-ion pairs are followed as a function of time. As in MC elastic and inelastic collisions between electrons and neutral molecules are included. The simultaneous calculation of the motions of 100 charged particles allows us to study the effects of collective interactions and external fields on the recombination process. Details of the simulation techniques are given in references [23-25].

Recombination in CO_2 , CH_4 , NH_3 and H_2O has been simulated by Monte Carlo. Results for electrons in CO_2 are shown in Fig. 3. Two body dissociative recombination, a curve crossing process,

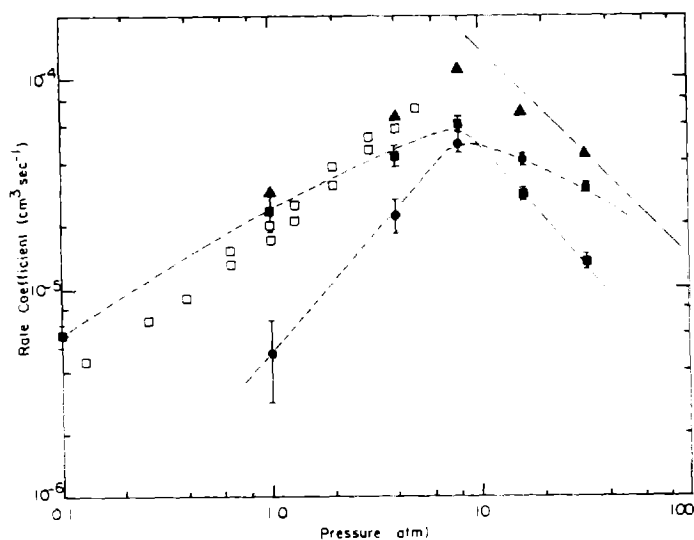


Figure 3. Recombination rate coefficients in CO_2 . Points \blacksquare and \bullet are the two body and three body contributions to the total (\blacktriangle) calculated coefficient. The points \square are the measured coefficients from Ref. [8]. The line --- is the diffusion limited rate, α_D .

is simulated by putting an absorbing sphere around the positive ion. The radius of the sphere is determined by matching the computed rate coefficient at very low pressure to a measured dissociative recombination rate coefficient. Three body recombination is said to have occurred when the total energy of an electron in the neighborhood of an ion falls below -12 kT. In Fig. 3 we see that the computed total rate coefficient agrees well with the measurements of Armstrong et al [8]. The two body recombination is seen to be enhanced by pressure effects, as has been postulated by Bates [26]. Collisions reduce the speed of an electron approaching an ion making it more likely to pass within the absorbing sphere and dissociatively recombine. Three body recombination dominates at higher pressures and eventually $\alpha \rightarrow \alpha_D$ as shown in Fig. 3. Similar results, in reasonable agreement with experiment [7,8], are obtained for recombination in NH_3 [23] and H_2O [24].

The computer simulations demonstrate the importance of energy exchange collisions in the recombination process,

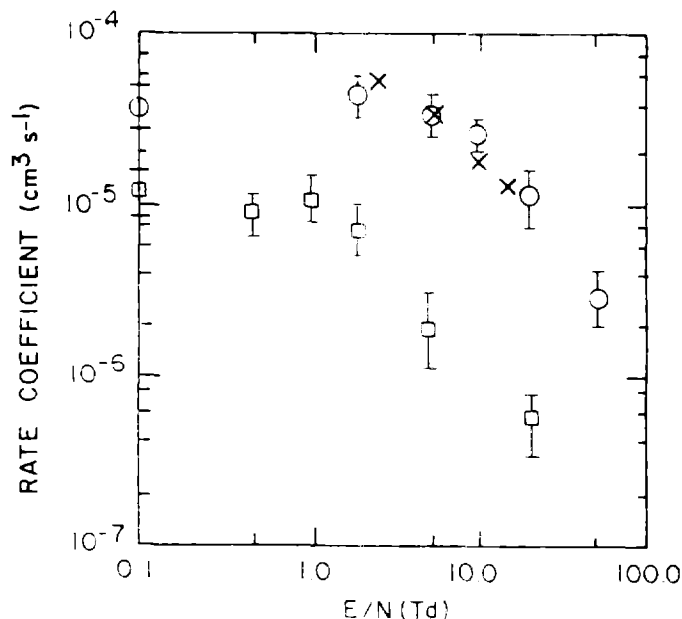


Figure 4. Computed total rate coefficient for recombination of electrons and ions in a discharge as a function of E/N for CO_2 (○) and CH_4 (□). The experimental results of Rev. [27] are denoted by the symbol X.

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as was discussed above in the development of $\alpha\alpha$ (v_u/N) (Eqn. 3). The MC calculations are, subject to the availability of good quality cross sectional data, quantitatively more accurate than Eqn. (3). There are exceptions, however, as we will see below in the discussion of recombination in CH_4 .

Littlewood, et al. [27,28] have measured recombination rates in $\text{CO}_2/\text{N}_2/\text{He}$ mixtures using a pulsed e-beam sustained discharge [29]. Knowledge of the e-beam ionization rate and the electron drift velocity along with measurement of discharge current yields the recombination rate. The measurements in CO_2 from Ref. [27] are plotted along with MD results [25] in Fig. 4 where we see excellent agreement.

Recombination at High Pressure: CH_4

Recently Nakamura, Shinsaka, and Hatano [30] (NSH) have measured the electron mobility and recombination rate coefficient in gaseous, liquid, and solid methane. Pulse radiolysis techniques [31] were used in the measurements. We see the rate coefficients measured by NSH plotted in Fig. 5 along with the MC calculations of Morgan [25]. For all but the very highest densities in the gas phase α is much less than α_p in both the measurements and the calculations. Except near the critical point, the calculations and the measurements disagree spectacularly. The calculations show α to peak at about $2 \times 10^{21} \text{ cm}^{-3}$. As pressure goes to zero the calculated α goes to the measured two body rate [4] of $3.9 \times 10^{-6} \text{ cm}^3/\text{sec}$. In the process of modeling an e-beam controlled discharge switch Kline [32] has estimated the recombination rate coefficient to be about $2 \times 10^{-6} \text{ cm}^3/\text{sec}$ for E/N values of a few Td. This estimate agrees with the MD calculation of α for CH_4 in an electric field as shown in Fig. 4.

At this point the reason for the great quantitative and qualitative difference between the measured and the calculated recombination rates is unknown. There are some possible theoretical causes. Examination of the static structure factor, $S(k=0)$, for CH_4 [23] shows that structure effects (significant pair correlations set in at densities of several times 10^{21} cm^{-3} . In addition, as Braglia and Dallacasa [34] have discussed, uncertainties in cross sectional data and high density effects conspire

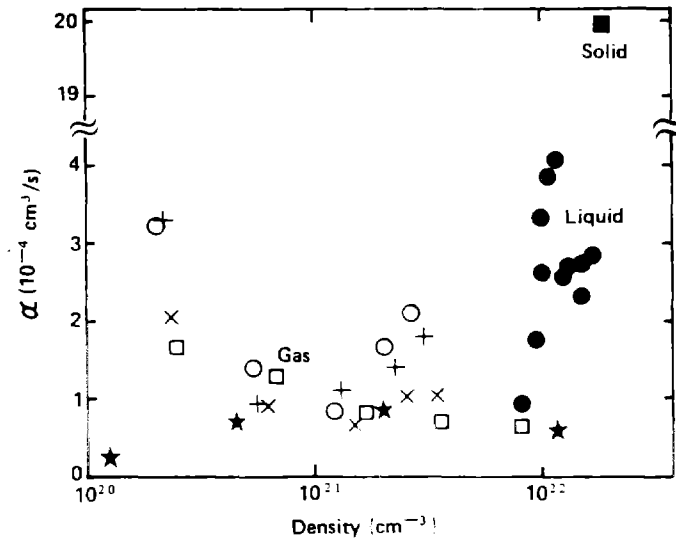


Figure 5. Recombination rate coefficients for electrons in methane. The points denoted by the symbol ★ are computed [25]. All the other points are measurements of Nakamura, et al. [30]. The gas phase measurements were performed at four temperatures ranging from 193 K to 295 K.

to make electron drift velocity quantitatively and qualitatively incorrect at densities as low as several times 10^{20} cm^{-3} . As the recent literature [35] on the subject demonstrates, the magnitude and energy dependence of the elastic cross section at low energy (especially near the Ramsauer minimum) is still very uncertain despite the numerous measurements of it dating back to 1925! There are enough theoretical uncertainties at these densities for us to be unable to state whether the difficulty is either experimental or theoretical. As a final note, unlike the situation with gas phase methane, recent MD simulations modeling recombination in liquid CH_4 [36] are in excellent agreement with the NSH measurements.

Summary

We see from the examples of CO_2 , NH_3 , and H_2O that the recombination process is reasonably well

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understood and modelable at low to moderate pressures. α_2 is enhanced by inelastic collisions with the neutral molecules. α_2 and α_3 are competitive with α_3 becoming dominant as pressure increases. At very high pressure, as we see with CH_4 , structure effects and probably clustering (which also affect transport coefficients) make quantitative modeling difficult.

Acknowledgements

I wish to thank Prof. Y. Hatano and Dr. A. V. Phelps for helpful discussions. This work was performed in part under the auspices of the U.S. Department of Energy at the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

References

- [1] Mitchell, J.B.A.; McGowan, J. Wm. In "Physics of Ion-Ion and Electron-Ion Collisions"; Brouillard F.; McGowan, J. Wm., Eds; Plenum: New York, 1982.
McGowan, J. Wm; Mitchell, J.B.A. In "Electron-Molecule Interactions and Their Applications"; Christophorou, L. G., Ed.; Academic Press: Orlando, 1984; Volume 2, Chapter 2.
- [2] Bates, D. R.; Khare, S. P. Proc. R. Soc. (London) 1965, 85, 231.
- [3] Bates, D. R.; Malaviya, V.; Young, N. A. Proc. R. Soc. (London) 1971, 320, 437.
- [4] Maier, H. N.; Fessenden, R. W. J. Chem. Phys. 1975, 62, 4790.
- [5] Flannery, M. R. In "Atomic Processes and Applications"; Burke, P. G.; Moiseiwitsch, B. L., Eds; North-Holland: Amsterdam, 1976; Chapter 12.
- [6] Bates, D. R. In "Advances in Atomic and Molecular Physics"; Bates, D. R.; Bederson, B., Eds; Academic Press: Orlando, 1985; Volume 20.
- [7] Warman, J. M.; Sennhauser, E. S.; Armstrong, D. A. J. Chem. Phys. 1979, 70, 995.
- [8] Armstrong, D. A.; Sennhauser, E. S.; Warman, J. M.; Sowada, U. Chem. Phys. Lett. 1982, 86, 281.
- [9] Bates, D. R. J. Phys. B 1975, 8, 2722.
- [10] Bates, D. R. J. Phys. B 1983, 16, L295.
- [11] Phelps, A. V. unpublished 1979; private communication.

- [12] Massey, H.S.W.; Gilbody, H. B. "Electronic and Ionic Impact Phenomena, 2nd Edition"; Oxford: London, 1974; V. 4, p. 2149.
- [13] Pitaevskii, L. P. Sov. Phys. JETP, 1962, 15, 5. Lifshitz, E. M.; Pitaevskii, L. P. "Physical Kinetics"; Pergamon Press: Oxford, 1981; Section 24.
- [14] Frost, L. S.; Phelps, A. V. Phys. Rev. 1962, 127, 1621.
- [15] Beaty, E. C.; Dutton, J.,; Pitchford, L. C. "A Bibliography of Election Swarm Data"; University of Colorado, Joint Institute for Laboratory Astrophysics Report No. 20, 1979.
- [16] Phelps, A. V. In "Electrical Breakdown and Discharges in Gases"; Kunhardt, E. E.; Luessen, L. H., Eds.; Plenum: New York, 1981; Part A.
- [17] Gousset, G.; Sayer, B.; Berlande, J. Phys. Rev. A 1977, 16, 1070.
- [18] Johnson, A. W.; Gerardo, J. B. Phys. Rev. A 1972, 5, 1410.
- [19] Borodin, V. M. Opt. Spectrosc. 1975, 38, 266.
- [20] Collins, C. B. Phys. Rev. 1969, 177, 254.
- [21] Deloche, R. Centre d'Etudes Nucle'aires de Saclay Report CEA-R-3450 1968.
- [22] Whitten, B. L.; Downes, L. W.; Wells, W. E. J. Appl. Phys. 1981, 52, 1255.
- [23] Morgan, W. L.; Bardsley, J. N. Chem. Phys. Lett. 1983, 96, 93.
- [24] Morgan, W. L. J. Chem. Phys. 1984, 80, 4564.
- [25] Morgan, W. L. Phys. Rev. A 1984, 30, 979.
- [26] Bates, D. R. J. Phys. B 1981, 14, 3525.
- [27] Littlewood, I. M.; Cornell, M. C.; Clark, B. K.; Nygaard, K. J. J. Phys. D 1983, 16, 2113.
- [28] Littlewood, I. M.; Cornell, M. C.; Nygaard, K. J. J. Chem. Phys. 1984, 81, 1264.
- [29] Douglas-Hamilton, D. H. J. Chem. Phys. 1973, 58, 4820.
- [30] Nakamura, Y.; Shinsaka, K.; Hatano, Y. J. Chem. Phys. 1983, 78, 5820.
- [31] Wada, T.; Shinsaka, K.; Namba, H.; Hatano, Y. Can. J. Chem. 1977, 55, 2144.
- [32] Kline, L. E. IEEE Trans. Plasma Sci. 1982, 10, 224.
- [33] Christophorou, L. G.; McCorkle, D. L. Chem. Phys. Lett. 1976, 42, 533.
- [34] Braglia, G. L.; Dallacasa, V. Phys. Rev. A 1982, 26, 902.
- [35] Ferch, J.; Granitza, B.; Raith, W. J. Phys. B 1985, 18, L445.
- [36] Morgan, W. L. J. Chem. Phys. 1986, to be published.